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## Selective Hydrogenation of CO<sub>2</sub> Dictated by Isomers in Au<sub>28</sub>(SR)<sub>20</sub> Nanoclusters: Which One is Better

#### Jiayu Xu,<sup>[a]</sup> Mingyang Chen,\*<sup>[b]</sup> and Yan Zhu\*<sup>[a]</sup>

**Abstract:** It is a challenge to make clear how isomerism in a heterogeneous catalyst induces distinct differences in catalytic properties, as attainment of the structural isomerism in a conventional catalyst is difficult. By successfully identifying the isomerism in the atomically precise Au nanoclusters, an exciting opportunity for unravelling catalysis of isomeric catalysts is opened up. Herein, we report that the isomerism in the Au<sub>28</sub>(SR)<sub>20</sub> nanoclusters with different surface atom arrangment can indeed render different catalytic behaviours in the selective hydrogenation of CO<sub>2</sub>. We anticipate that our studies will serve as a starting point for fundamental investigations about how to control the catalytic activity and selectivity by the isomerism-induced catalysis.

Isomers with the same molecular formula but different atomistic arrangements are of special concerns in the organic and biological chemistry, due to the possibly distinct differences in their physical and chemical properties.<sup>[1]</sup> Owing to the inherent heterogeneity of the practical catalysts, however, it is not clear yet whether the structural isomerism also exists in heterogeneous catalysts. If so, a fundamental question is to be addressed: do isomers of catalysts exhibit similar or different catalytic behaviors? At nanoscale, a subtle change in the geometry of a catalyst can have large impacts on the catalytic performance, and the catalytic activity and selectivity can strongly rely on the atomistic arrangement of a catalyst.<sup>[2]</sup> Therefore, it is very interesting to unveil isomerism-induced catalysis for the heterogeneous catalysts, which will enhance the diversity of heterogeneous catalysis. Yet such tasks are extremely challenging, mainly because the discovery and identification of structural isomerism in the catalysts are difficult by conventional characterization techniques.

Fortunately, with recent advances on atomically precise metal nanoclusters, identification of the structural isomerism becomes possible. Recently, isomerism in the  $Au_n(SR)_m$  nanoclusters was successfully discovered.<sup>[3]</sup>  $Au_n(SR)_m$  nanoclusters are ideally composed of an exact number of atoms and behave like molecules.<sup>[4]</sup> The isomerism of  $Au_n(SR)_m$  nanoclusters allows us to discover unknown catalysis for new isomers of the heterogeneous catalysts, which is typically not possible for the traditional catalysts.

In this work, two isomers of  $Au_{28}(SR)_{20}$  nanoclusters are used as model catalysts to catalyze the selective hydrogenation of CO<sub>2</sub>. The two isomers,  $Au_{28}(SPh-Bu)_{20}$  (Ph-Bu = 4-tertbutylphenyl) and  $Au_{28}(SC_6H_{11})_{20}$  (C<sub>6</sub>H<sub>11</sub> = cyclohexyl), have the same face-centered-cubic  $Au_{20}$  kernel but different

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arrangements of surface atoms: the remaining eight gold atoms and twelve ligands form two trimetric staples in Au<sub>28</sub>(SPh-Bu)<sub>20</sub> (Figure 1A), while the eight gold and twelve ligands are arranged into two trimeric staples and two monomeric staples in Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub> (Figure 1B).<sup>[3a,3b]</sup> Despite the two isomeric Au<sub>28</sub>(SR)<sub>20</sub> differ only by an eight-gold-atom arrangment, drastic differences in their catalytic proformances for the selective hydrogenation of CO<sub>2</sub> are observed. The investigation offers new insights into the isomerism-induced catalysis at the unprecedented level of atomic precision.



Figure 1. Isomers in Au<sub>28</sub>(SR)<sub>18</sub>: (A) Au<sub>28</sub>(SPh-Bu)<sub>20</sub> and (B) Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>. The Au<sub>20</sub> kernels (upper panel) and the Au<sub>28</sub>S<sub>20</sub> frameworks (lower panel). Color labels: Au, green; S, magenta. C and H are omitted for clarity.

The compositions of the two nanoclusters were determined by matrix-assisted laser desorption ionization mass spectrometry (Figure S1), confirming that the nanoclusters are both composed by 28 gold atoms that are protected by twenty thiolate ligands. The blue shifts of the UV-vis absorption bands were found for Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>, with respect to the spectrum for Au<sub>28</sub>(SPh-Bu)<sub>20</sub>; similar HOMO-LUMO gaps were observed for Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub> and Au<sub>28</sub>(SPh-Bu)<sub>20</sub>, which is attributed to the two clusters sharing the same Au<sub>20</sub> kernels (Figure S2).<sup>[3a,3b]</sup>

Considering the importance of an effective conversion of CO2 into liquid fuels for mitigating global warming and energy supply problems,<sup>[5]</sup> the selective hydrogenation of CO<sub>2</sub> was used as a pivotal reaction to gain insights into catalysis of isomers in Au<sub>28</sub>(SR)<sub>20</sub>. As shown in Figure 2A and 2B, Au<sub>28</sub>(SPh-Bu)<sub>20</sub> was more effective than  $Au_{28}(SC_6H_{11})_{20}$  for the catalytic hydrogenation of CO2. The conversion rate of CO2 over  $Au_{28}(SPh-Bu)_{20}$  was faster than that over  $Au_{28}(SC_6H_{11})_{20}$ . More interestingly, the isomeric Au<sub>28</sub> nanoclusters can exhibit different selectivity for products. The conversion of CO<sub>2</sub> to methanol was achieved over Au<sub>28</sub>(SPh-Bu)<sub>20</sub> (Figure 2A), whereas over  $Au_{28}(SC_6H_{11})_{20}$  both methanol and methyl formate were obtained as major products with a mole ratio of ~2:1 between methanol and methyl formate (Figure 2B). Notably, other than the methane by-product, CO, a common by-product in the reaction over practical Cu-ZnO catalysts, that is responsible for poor methanol selectivity, was not found in the two Au<sub>28</sub> systems. Base on the turnover frequency (TOF) of the two clusters for CO<sub>2</sub> hydrogenation at different reaction temperatures, it is found that the apparent activation energy of the Au<sub>28</sub>(SPh-Bu)<sub>20</sub>

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catalyst was lower than that of the  $Au_{28}(SC_6H_{11})_{20}$  catalyst (Figure 2C).



Figure 2. Catalytic performance of  $CO_2$  hydrogenation over isomeric Au<sub>28</sub>(SR)<sub>18</sub> catalysts: (A) Au<sub>28</sub>(SPh-Bu)<sub>20</sub> and (B) Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>. (C) Corresponding Arrhenius plots. (D) Comparison experiments with different reaction gas. (E) Comparison of catalytic properties of Au<sub>28</sub>(SR)<sub>20</sub> catalysts with different pretreatments. (F) Catalytic results of Au<sub>18</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>14</sub> and Au<sub>44</sub>(SPh-Bu)<sub>28</sub> for CO<sub>2</sub> hydrogenation. Reaction conditions; 2 MPa CO<sub>2</sub>/H<sub>2</sub> (1:3), 130 °C, 24 h. Au<sub>28</sub>T: Au<sub>28</sub>(SPh-Bu)<sub>20</sub> and Au<sub>28</sub>C: Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>.

The two isomers showed an excellent durability and the CO<sub>2</sub> conversion and product selectivity in the cycles of the reused catalysts were comparable with the first run results (Figure S3). We compared the UV-vis spectroscopic fingerprints of the fresh and used catalysts and no obvious spectral change was observed (Figure S4). The retention of characteristic optical spectra after reactions ruled out the possibility for Au<sub>28</sub>(SR)<sub>20</sub> decomposition under the reaction conditions. Transmission electron microscopy studies showed that the two nanoclusters had no obvious aggregation throughout the reactions (Figure S5). Considering isomers themselves containing carbon sources (ligands), the comparison experiments were carried out; when no reaction gas was introduced, no product was obtained; with either CO<sub>2</sub> or H<sub>2</sub> being introduced, no product was detected (Figure 2D), indicating that the products derive from the reaction of CO<sub>2</sub> and H<sub>2</sub> rather than organic ligands. To study the effect of the thiolate ligands on the catalytic performance, the catalysts were pretreated at 400 °C (above ligand desorption temperature, Figure S6) to remove all the thiolate ligands, leaving exposed Au(0) atoms on the surface of particles. From Figure 2E, the reactivity of the bare gold catalysts decreased and the major product was CH<sub>4</sub>, suggesting that underlying reaction pathway may have been changed. Moreover, the Au<sub>18</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>14</sub> nanoclusters (where  $C_6H_{11}$  = cyclohexyl) and the Au<sub>44</sub>(SPh-Bu)<sub>28</sub> nanoclusters (where Ph-Bu = 4-tert-butylphenyl) were

synthesized for further comparison (note that the corresponding UV-vis spectra and the atomic structures were shown in Figure S7). Although the  $Au_{18}(SC_6H_{11})_{14}$  catalyst was protected by the same ligand (SC<sub>6</sub>H<sub>11</sub>) with Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>, it exhibited different product selectivity from Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub> for CO<sub>2</sub> hydrogenation under identical reaction conditions, as shown in Figure 2F. As much, the Au<sub>44</sub>(SPh-Bu)<sub>28</sub> catalyst with same thiolate ligand (SPh-Bu) with Au<sub>28</sub>(SPh-Bu)<sub>20</sub> showed different catalytic performance for CO<sub>2</sub> hydrogenation: the products such as ethanol, methanol, formic acid and methane can be obtained over the former, while methanol and methane were produced on the latter (Figure 2F). These results clearly ruled out the ligand effects of the two Au<sub>28</sub>(SR)<sub>20</sub> catalysts on the performance of CO<sub>2</sub> hydrogenation. The catalytic properties are mainly determined by the atomic structure of gold atoms rather than thiolate ligands.

Attenuated total reflection infrared (ATR-IR) spectroscopy was conducted to detect the potential intermediates adsorbed over the two isomers in the hydrogenation reaction of CO<sub>2</sub>. Figure S8 shows ATR-IR spectra obtained from exposure of the isomers to a mixture gas of CO<sub>2</sub> and H<sub>2</sub>. The bands at 2962 and 2960 cm<sup>-1</sup> can be assigned to asymmetric CH stretches of methoxy groups produced by the reaction of methanol with catalysts, whereas the apparent bands at 2887 and 2886 cm<sup>-1</sup> were associated with formate.<sup>[6]</sup> A set of peaks at 1383, 1239, and 1056 cm<sup>-1</sup>, corresponding to methoxy species,<sup>[7]</sup> were observed for Au<sub>28</sub>(SPh-Bu)<sub>20</sub>, and the corresponding peaks were observed at 1383, 1241, and 1053 cm<sup>-1</sup> for Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>. The results imply that the methoxy is the major intermediate in the hydrogenation of CO<sub>2</sub> catalyzed by the two isomers.

The difference in the catalytic selectivity toward methanol for the two isomers is understood by the chemical desorption capacity of methanol onto the two isomeric catalysts. The methanol-temperature-programmed desorption was carried out and the temperature was ramped to 300 °C (note that higher temperatures were not allowed because it might lead to decomposition and aggregation of nanoclusters following the ligands desorption which can be deduced from Figure S6). As shown in Figure S9, the peaks of methanol desorption were located at 197 °C for  $Au_{28}(SPh\text{-}Bu)_{20}$  and 210 °C for  $Au_{28}(SC_6H_{11})_{20}$ , suggesting that  $Au_{28}(SPh-Bu)_{20}$  favors the leave of methanol from the active sites. In particular, the asymmetric shape of the desorption peak of methanol over Au<sub>28</sub>(SPh-Bu)<sub>20</sub>, which implies a first order desorption kinetics,[8] indicates that the adsorption of methanol over the Au<sub>28</sub>(SPh-Bu)<sub>20</sub> is nondissociative. In contrast, the symmetric methanol desorption peak over Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub>, which is associated with the second order desorption kinetics,[9] implies that the adsorption of methanol over Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub> is dissociative. It is proposed that the differences in the desorption capacity of methanol onto the isomeric Au<sub>28</sub>(SR)<sub>20</sub> may partially account for the different selectivity of methanol on the two catalysts.

D/H and H/D exchange studies are shown in Figure S10. During the first run of D/H exchange (black and red curves; note that the two isomers were pretreated in the Ar at 150 °C for 1h and then D<sub>2</sub> was introduced to exchange with H species), H species associated with the two Au<sub>28</sub> catalysts are identical and assigned to the H of organic ligands. Immediately after the exchange of D<sub>2</sub> with H species of ligands and the cooling of catalysts under a D<sub>2</sub> stream, H<sub>2</sub> was introduced to perform the second run of H/D exchange. The new peaks (blue and pink curves) were observed (284 °C for Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub> and 371 °C for Au<sub>28</sub>(SPh-Bu)<sub>20</sub>), which are tentatively ascribed to the

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chemically adsorbed deuterium on the gold sites.<sup>[10]</sup> Deduced from the second run of H/D exchange results,  $Au_{28}(SC_6H_{11})_{20}$ was easier to adsorb and activate H<sub>2</sub> compared to  $Au_{28}(SPh-Bu)_{20}$ . However, the results deviated from the above catalytic results. One possible answer is that the true active species are no longer the original clusters at the high temperatures of H/D experiments. Interestingly, the H/D exchange results can account for the catalytic performance of the catalysts pretreated at 400 °C. The structures of the pretreated nanoclusters decomposed and the Au surface atoms were exposed, in which the ligand-off  $Au_{28}(SC_6H_{11})_{20}$  was easier to adsorb and activate H<sub>2</sub> (Figure S10) and thus exhibited higher activity for CO<sub>2</sub> hydrogenation than the ligand-off  $Au_{28}(SPh-Bu)_{20}$  (Figure 2E).



**Figure 3.** DFT calculation: (A) hydrogenation energy for Au-thiol bond of  $Au_{28}C$  and  $Au_{28}T$ . The hydrogenated catalysts (B) with a RS-H-Au moiety and (C) with an Au-(H)-Au moiety. Color code: orange: surface Au; purple interior Au; yellow: S.

To further understand catalysis of the two isomeric Au<sub>28</sub> catalysts, density functional theory (DFT) calculations were performed. A simplified computational model, where the thiolates were replaced with SCH<sub>3</sub>, was used for each Au<sub>28</sub> catalyst; therefore, the two clusters share the same formula, Au<sub>28</sub>(SCH<sub>3</sub>)<sub>20</sub>. To distinguish the two Au<sub>28</sub>(SCH<sub>3</sub>)<sub>20</sub> clusters, the simplified Au<sub>28</sub>(SC<sub>6</sub>H<sub>11</sub>)<sub>20</sub> is denoted as Au<sub>28</sub>C and the simplified Au<sub>28</sub>(SPh-Bu)<sub>20</sub> is denoted as Au<sub>28</sub>T. Due to the point group symmetries of the structures, there are 9 distinct types of Au sites in Au<sub>28</sub>C and 8 types of Au sites in Au<sub>28</sub>T (Figure 3A). Au<sub>28</sub>C contains three types of Au<sub>x</sub>(SR)<sub>x+1</sub> staples with 10 distinct Au-thiolate (Au-SR) bonds, and Au<sub>28</sub>T contains two types of staples with 10 distinct Au-SR bonds. First, we analyzed the site activities for all the Au-SR moieties in Au<sub>28</sub>C and Au<sub>28</sub>T (Figure 3A), as H<sub>2</sub> adsorption and activation are prerequistes for reduction of CO<sub>2</sub> on metal catalysts. H<sub>2</sub> can dissociate and react with the Au-SR bonds with low endothermicities (endothermic by 10-20 kcal/mol, Figure 4A), resulting in a hydrothiolate (HSR) moiety and a hydrogold (AuH) moiety. Note that the surface HSR only exists transiently. It continues to either form a RS-H-AuH moiety with AuH (Figure 3B), which repairs the cleavage of the staple, or to desorb from the catalyst, acompanied by formation of Au-(H)-Au moiety (Figure 3C). All of the Au-SR moieties of Au<sub>28</sub>T and most of the Au-SR moieties of Au<sub>28</sub>C tend to form RS-H-AuH with H<sub>2</sub>. Only two Au-SR moieties, Au(3)-SR and Au(9)-SR (the labels of Au atoms are in Figure 3A), of Au<sub>28</sub>C form Au-(H)-Au with H<sub>2</sub> with endothermicities of 12.4 and 9.7 kcal/mol, respectively. Natural atomic charge analysis of Au<sub>28</sub>C and Au<sub>28</sub>T (Figure S11) reveals that RS-H-AuH or Au-(H)-Au might be related to the metallicity of the two Au atoms in Au-SR-Au in the raw catalyst. The formation of Au-(H)-Au seems to occur when the one of the two Au atoms is highly positively charged, and the other is slightly negatively charged, as seen in the Au(2)-SR-Au(9) and Au(3)-SR-Au(9). Such charge separation might acount for the formation of Au-Au bond in Au-(H)-Au and the desorption of HSR.



Figure 4. Potential energy surfaces (A) for formation of CH<sub>3</sub>OH at a RS-H-Au site of hydrogenated  $Au_{28}T$  and (B) for formation of HCOOCH<sub>3</sub> at a  $Au_3H_2$  site of hydrogenated  $Au_{28}C$ .

 $Au_{28}C$  has a  $D_2$  point group symmetry, and therefore Au-(H)-Au can be formed at both sides on Au(3) and Au(9) of  $Au_{28}C$ , leading to two doubly hydrogenated Au<sub>3</sub> triangle sites. The two hydrides of Au<sub>3</sub>H<sub>2</sub> can reduce 2 CO<sub>2</sub> molecules, which might lead to the reaction product containing 2 C atoms (2C product). Note that unlike Au(3) of Au<sub>28</sub>C, Au(9) is not a surface Au where the two hydrides at Au(9) is separated by the 3 Au atoms of the outmost Au<sub>3</sub>(SR)<sub>4</sub> staple, implying that 2C product is not likely to be formed at Au(9). Potential energy surfaces for  $CO_2$ hydrogenation reaction at a RS-H-Au site of hydrogenated Au<sub>28</sub>T and an Au<sub>3</sub>H<sub>2</sub> moiety of hydrogenated Au<sub>28</sub>C were calculated at the DFT level and compared. At the RS-H-Au site, methanol can be formed with a total reaction:  $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ , via -COOH, -CHO, and -OCH<sub>3</sub> mono-adsorption complexes (Figure 4A). The two hydrides of the Au<sub>3</sub>H<sub>2</sub> site of hydrogenated Au<sub>28</sub>C can react with 2 CO<sub>2</sub> to form Au<sub>3</sub>(COOH)<sub>2</sub> (Figure 4B). The two COOH adsorb at the same asymmetric sites as the two hydrides, forming a terminal ligand and a bridge ligand. No coupling reaction products were found for the two adsorbed COOH. The COOH ligands can be further reduced to form two CHO. The bridge CHO, like the bridge COOH, have an orientation potentially favoring ligand-ligand coupling, as the O and H atoms of CHO are confined in the C(HOAu<sub>2</sub>) tetrahedron so that the connecting path between the two CHO ligands are not blocked by O or H. The O of the terminal CHO can possibly couple with the C of the bridge CHO to form HC-O-CHO; this reaction step,

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however, is found to be endothermic by ~20 kcal/mol. More likely, CHO will be further reduced by H<sub>2</sub>. Formation of OCH<sub>3</sub> from CHO is mostly likely via a transition state with an AuOC triangle geometry.<sup>[11]</sup> Such a triangle geometry is less likely to be formed from the bridge CHO as compared to the terminal CHO case, as C of bridge CHO is more confined. Therefore, the bridge CHO is more difficult to be reduced than the terminal CHO, and a reaction intermediate with a terminal OCH3 and a bridge CHO will be first formed at the Au<sub>3</sub> active site. The coupling of OCH<sub>3</sub> and CHO to form methyl formate is found to be exothermic by 22.3 kcal/mol, while the ligand orientations are also favorable. The terminal OCH3 might also form methanol in an alternative reaction path, similar to the final reaction step at the RS-H-Au site (Figure 4A) with an exothermcity of ~23 kcal/mol, but this path is expected to be less kinetically favorable as additional hydrogen activation is required.

In summary, we have explicitly revealed that the structural isomerism in the  $Au_{28}(SR)_{20}$  nanoclusters impacts the catalytic properties, as demonstrated in the selective hydrogenation of CO<sub>2</sub>. The results of the present study shed light on the intriguing role of the surface-atom arrangement in tuning the catalytic activity and selectivity, which will not only open up future exciting opportunities for understanding the origin of isomerism-induced catalysis but also expand the horizons of structural isomer catalysts.

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Keywords: isomer • Au<sub>28</sub> • nanoclusters • atomicity • catalysis

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It is unclear whether and how isomerism in a catalyst affect the catalytic performance. Here we demonstrate that the structural isomerism in  $Au_{28}(SR)_{20}$  really renders distinct catalytic behaviour to the selective hydrogenation of CO<sub>2</sub>. The isomerism-induced catalysis provides guidances for how to control the catalytic activity and selectivity by the position arrangement of atoms in catalysts.



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